Macromolecules **1991,** *24,* 2231–2235

Compatibilizing Effect of a Styrene–Methyl Methacrylate Block Copolymer on the Phase Behavior of Poly(2,6-dimethyl-1,4-phenylene oxide) and Poly(styrene-*co*-acrylonitrile) Blends

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Received March 14, 1990; Revised Manuscript Received October 22, 1990

ABSTRACT: The effect of poly(styrene-*b*-methyl methacrylate) block copolymer on the phase behavior of an immiscible polymer pair, poly(2,6-dimethyl-1,4-phenylene oxide) (MPPO) and poly(styrene-*co*-acrylonitrile) (SAN), was examined in terms of phase structure and thermal properties. The block copolymer was prepared by sequential anionic polymerization of styrene and methyl methylacrylate and blended with two polymers by precipitation. Scanning electron micrographs show that the blends exhibit a more regular and finer dispersion as the block copolymer is added. Thermal analysis with the aid of physical aging reveals that the block copolymer is located at the interface.

Introduction

Polymer blends as the simplest route for combining outstanding properties of different existing polymers have been of considerable interest.[1-3] Because the combinatorial entropy of mixing of two polymers is drastically smaller than that of low-molecular-weight compounds and the enthalpy of mixing is often a positive quantity or near zero, it is thermodynamically unfavorable for most polymers to form homogeneous mixtures. In order to overcome this difficulty various methods, such as the introduction of a functional group that gives a specific interaction (hydrogen bonding, ion–ion interaction, etc.) between immiscible polymer pairs, have been attempted.[4-10]

With the great interest in blends of homogeneous phase structure (e.g., Noryl), there has recently been a good deal of interest in the studies of the structure and properties of heterogeneous multicomponent polymer mixtures, wherein each of the components retains its own properties and then sum up in a final product that may also display some new features due to the particular phase morphology. In such systems, however, two structural requirements are necessary to secure adequate overall physicomechanical behavior. One is a proper interfacial tension leading to a phase size small enough to allow the material be considered as macroscopically homogeneous. The other is an interfacial adhesion strong enough to assimilate stresses and strains without disruption of the established morphology. However, most immiscible polymer blends do not meet these demands.

The method giving interfacial activity by using block or graft copolymers has developed gradually with time. In general, when an AB block or graft copolymer is added to an A/B binary blend, thus forming an A/B/AB ternary blend (where A and B are two immiscible polymers), the following major effects are observed: higher degree of dispersion, better adhesion between phases and stabilization of microphase against coalescence.

Heikens et al.[11] observed that the dimensions of the polyethylene domains in polystyrene (PS)/polyethylene (PE) blends are reduced when a graft copolymer is added. Similar results were obtained for poly(vinyl chloride) (PVC)/polyethylene (PE)/chlorinated polyethylene (CPE) blends by Paul et al.[12,13] and for polyamide/polyolefin blends by Braun and Eisenlohr.[14]

According to more recent reports,[15] molecular architecture and segmental molecular weight of the AB copolymer play an important role in determining the emulsifying efficiency. The simpler the architecture, the easier is the penetration of segments into the respective homopolymer phases. Consequently, block copolymers are expected to be more efficient than graft copolymers, and diblock copolymers should be superior to triblock ones.

Early efforts were concentrated on blends of block copolymers with homopolymers having repeat units identical with each block of the copolymer. Studies of the PS/low-density polyethylene (LDPE)/hydrogenated poly(styrene-*b*-butadiene) system are examples of this case.[16-19] More recently, the validity of the approach using a polymer emulsifier (AC block copolymer) to bridge the incompatibility gap between two polymers A and B (where polymer C is miscible with polymer B) has been reported. Ouhadi et al.[20] examined the concept for the poly(vinylidene fluoride) (PVDF)/Noryl/poly(styrene-*b*-methyl methacrylate) system. However, to our knowledge, there has been no report on blends of two immiscible polymers (A and B) and a CD diblock copolymer (poly(C-*b*-D)), where A and B are miscible with C and D, respectively.

In fact, the mixing of a block copolymer with homopolymers having identical units is thermodynamically athermal process. Several experimental investigations[21,22] have shown that the molecular weights of the individual segments of a copolymer have to be equal to or higher than those of the corresponding homopolymers. By contrast, when a block copolymer whose blocks are chemically different but miscible with the corresponding polymers is blended with two immiscilble polymers, an exothermic interaction between miscible pairs exists. This interaction can enhance the compatibilizing effect of the block copolymer. This concept is here applied to the blend system of two immiscible polymers, poly(1,4-dimethyl-2,6-phenylene oxide) (MPPO) and poly(styrene-*co*-acrylonitrile) (SAN) using styrene–methyl methacrylate block copolymer. MPPO/PS blend is miscible and has been produced commercially under the trade name Noryl. It is well-known that PMMA forms miscible blends with SAN over a limited window of comonomer compositions. Fowler et al.[23] examined the effect of copolymer composition on the miscibility of SAN with PMMA and they obtained optically clear blends for the copolymers having an AN content of 9.5–28.0 wt %. In general, an exothermic heat of mixing between two polymers is recognized as a requirement for their miscibility.[15] Paul and Barlow[24]

0024-9297/91/2224-2231$02.50/0

Table I
Molecular Characteristics of the Polymer Samples

polymer	source	mol wt (M_w)	T_g, °C	remarks
poly(2,6-dimethyl-1,4-phenylene oxide) (MPPO)	General Electric Co.	35 000[a]	205.6	
poly(styrene-*co*-acrylonitrile) (SAN)	Ashai Chemical Co.	181 000	109.0	14.7% AN
poly(styrene-*b*-methyl methacrylate) (SbM)	synthesized	96 000[a]	104.0	64% ST[b]

[a] Measured by GPC. [b] Determined by elemental analysis.

proposed the binary interaction model, which suggests that this exothermic mixing may arise in mixtures with copolymers having a net intrachain repulsion between the comonomer units. Their calorimetry results for low-molecular-weight analogues show that the net interaction parameter B can be negative even in the case when all segmental interaction parameters B_{ij} are positive.[25]

In this paper, the effect of a styrene–methyl methacrylate block copolymer on the phase structure and compatibility of an immiscible blend of MPPO and SAN was examined by means of scanning electron microscopy and thermal analysis.

Experimental Section

Materials. Styrene and methyl methacrylate were washed with aqueous 5% sodium hydroxide to remove inhibitors and then with distilled water. After washing, they were dehydrated by using calcium hydride (CaH_2) with stirring for over 24 h. They were then distilled under reduced pressure into a flask containing freshly baked molecular sieves (4A). They were stored in a refrigerator and used within 3 days. Tetrahydrofuran (THF) was refluxed over calcium hydride for several hours and distilled into a flask containing lumps of sodium metal. To this was added naphthalene, and the mixture was refluxed until the sodium–naphthalene complex was formed, characterized by the appearance of a dark green color. This complex traps all impurities in THF. The sodium–naphthalene solution was distilled again into a flask containing freshly baked molecular sieves and then stored in a dark place in order to prevent peroxide formation by sunlight. Nitrogen gas was used as the polymerization atmosphere. Commercial high-purity nitrogen was repurified by passing through successive columns containing pyrogallol solution, dry sulfonic acid, phosphorus pentoxide (P_2O_5), and molecular sieves (4A).

Polymerization. All glassware was steeped in a dry sulfuric acid bath for 2 days and then washed exhaustively. The glassware was then dried at high temperature and cooled carefully in a desiccator. A flask containing a magnetic stirrer bar was sealed with a rubber stopper and purged with purified nitrogen gas. A mesured amount of THF was fed by syringe. Then styrene monomer was fed and the reactor was placed in a constant-temperature bath (dry ice–acetone bath, –78 °C). The solution was agitated with the magnetic stirrer. Upon dropwise addition of the measured quantity of the initiator, the deep red color of polystyrene developed, which disappeared immediately upon addition of methyl methacrylate monomer. Finally, the polymerization was quenched by adding methanol. The polymer solution was diluted with THF and then poured into an excess of methanol to give a white powder precipitate. The precipitate was filtered and dried under vacuum at 50 °C for 2 days.

Polymer Characterization. The polymer solution was clear and homogeneous, which is evidence of formation of a block copolymer, since simple mixtures of PS and PMMA make turbid solutions and phase separation occurs when the solution is kept without agitation for several hours. The block length was determined by measuring the mole fraction of styrene by elemental analysis (CHN-Code, Yanaco MT2). The (relative) weight-average molecular weights of the polymers were measured by gel permeation chromatography (GPC, Waters Associates) with THF as eluent.

Blending. MPPO and SAN were obtained from General Electric Co. and Asahi Chemical Co., respectively. Table I lists the properties of the polymers. The block copolymer and two polymers were blended by precipitation from 5% chloroform solution into a large quantity of methanol. All the precipitates were filtered and dried under vacuum at 50 °C for 2 days.

Electron Microscopy. Blend samples were compression molded into sheets at 250 °C, which is lower than the reported lower critical solution temperatures of MPPO/PS and SAN/PMMA.[23] The sheets were fractured at liquid nitrogen temperature, and the fracture surface was treated with acetone at room temperature for 30 min to remove the SAN domain. The surface was coated with gold and observed with a scanning electron microscope (SEM, JEOL JSM-35). The accelerating voltage was 25 kV.

Thermal Analysis. Thermal analysis was carried out in a Du Pont 910 differential scanning calorimeter (DSC). Depending upon the composition, samples were first heated to 150 or 250 °C at a rate of 20 °C/min and maintained for 3 min to destroy thermal history. They were then cooled to 60 °C and reheated to 150 or 250 °C at a rate of 20 °C/min. Only the second-run data were accepted. When annealing was required, the samples were annealed at 82 °C for 145 h. Annealed samples were heated to 150 or 250 °C at a rate of 10 °C/min. In this case, the first-run data were accepted.

Results and Discussion

It is generally known that the block copolymer should be located at the interface of two immiscible polymers and that each block of the copolymer has to penetrate into the corresponding polymer domains for the block copolymer to play a proper role as an interfacial agent.

Figures 1 and 2 show the morphology changes of MPPO/SAN blends as the block copolymer is added. When two immiscible polymers, MPPO and SAN, were blended without block copolymer, phase separation took place as expected (see Figures 1A and 2A). They formed very large, coarse, and irregular phases. However, when a small amount of the block copolymer was added to the blends, more regular and finer dispersion could be observed (see Figures 1B and 2B). From this result, it is believed that the block copolymer, poly(styrene-*b*-methyl methacrylate) (SbM), favors the dispersion of the blends.

It is important to ascertain whether the block copolymer is located suitably at the interface and that each block is dissolved into the corresponding domains. The location of the block copolymer could be elucidated by examining the composition of each phase. Thermal analysis was employed to obtain informations on the phase structure.

Figure 3 shows differential scanning calorimetry (DSC) thermograms of MPPO/block copolymer binary blends. As shown in the figure, the block copolymer lowers the glass transition temperture of the MPPO domain. Since only the polystyrene block is dissolved in the MPPO domain, the lowering of T_g indicates that the polystyrene block is dissolved in the MPPO domain. For the block copolymer, only a single glass transition temperature is observed because of the closeness of T_g of the two blocks, 118 °C for PMMA and 107 °C for PS.

DSC thermograms of SAN/block copolymer binary blends are presented in Figure 4. As the amount of block copolymer in the blend is increased, two T_g's are observed, indicating that the blends have two-phase structures. The upper T_g corresponds to the domain composed of SAN and the penetrating PMMA block of the copolymer, and the lower T_g corresponds to the PS phase of the copolymer.

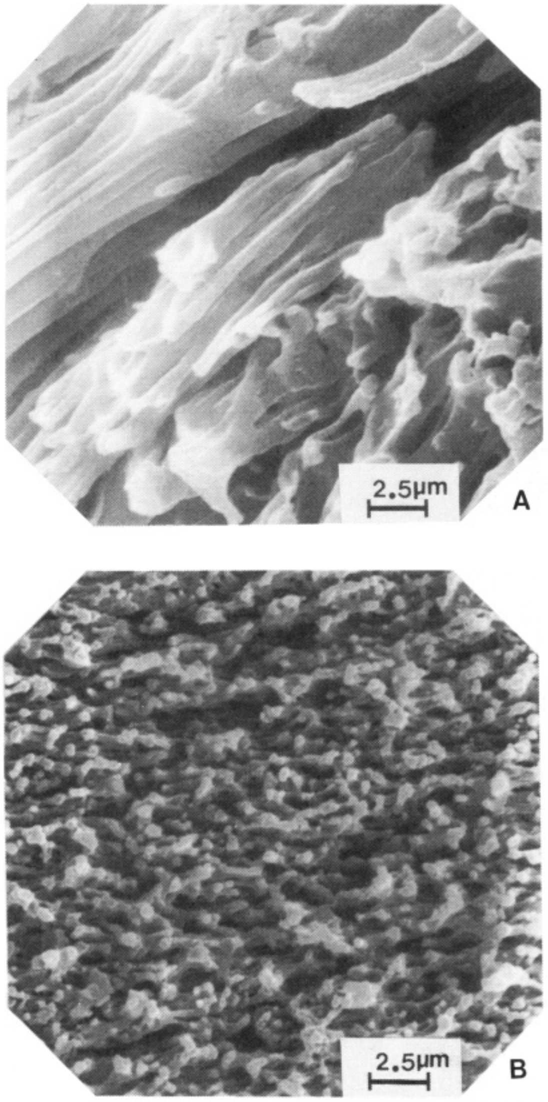

Figure 1. Scanning electron micrographs of 50/50 MPPO/SAN blends: (A) without block copolymer; (B) 4% block copolymer added.

It is noteworthy that the AN content of SAN used in this study was 14.7 wt %, which lies within the miscible region reported by Fowler et al.[23]

In the case of a blend of two immiscible polymers where their respective T_g's are very close, it is difficult to distinctly observe two separate glass transition temperatures by general thermal analysis. Recently, the nature of the physical aging process common to glassy materials was recognized by many workers[26-28] to solve such a problem. When an amorphous material is quenched from the rubbery to the glassy state, it is in a nonequilibrium state. Annealing the quenched material below the glass transition temperature results in relaxation toward equilibrium and a corresponding change in thermodynamic quantities such as enthalpy and volume. The decrease in enthalpy is recovered during reheating and characterized by an endothermic peak at the temperature ranging from well below to the upper edge of the glass transition temperature.

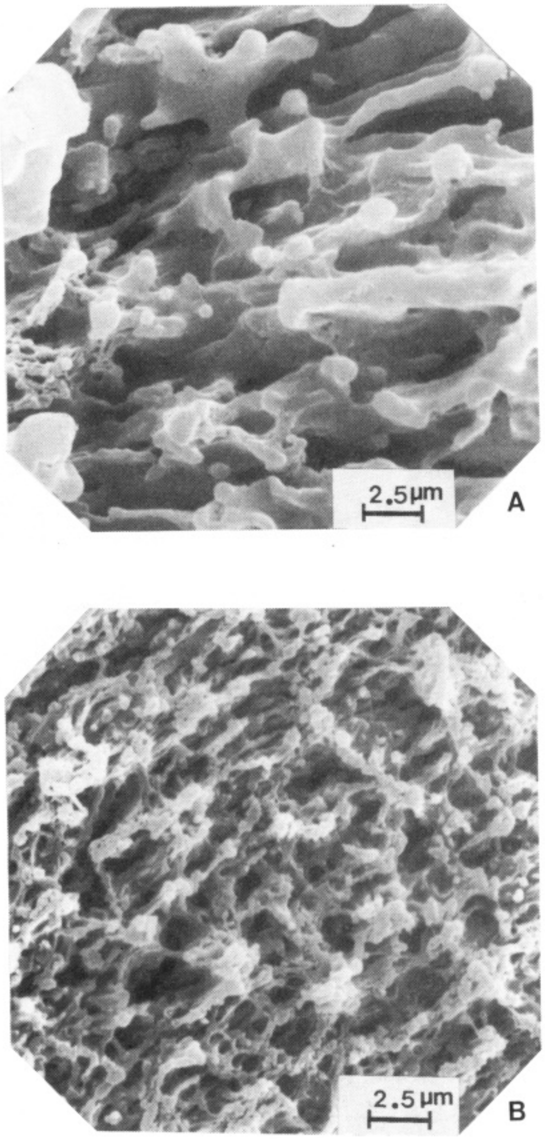

Figure 2. Scanning electron micrographs of 70/30 MPPO/SAN blends: (A) without block copolymer; (B) 1% block copolymer added.

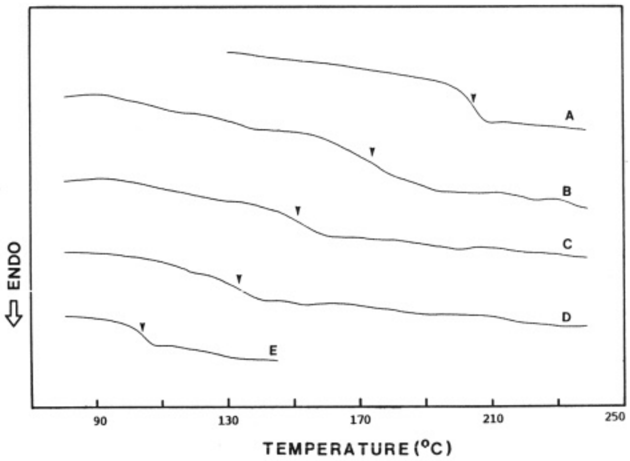

Figure 3. DSC thermograms of MPPO/SbM binary blends: (A) MPPO; (B) 70/30 MPPO/SbM; (C) 50/50 MPPO/SbM; (D) 30/70 MPPO/SbM; (E) SbM.

Figure 5 shows DSC scans for the binary blends of SAN/block copolymer when aged at 82 °C for 145 h. For the block copolymer (Figure 5A), two separate peaks are observed. Figure 5A is comparable with the DSC thermogram of Figure 3E. The upper small and broak peak in Figure 5A corresponds to the PMMA block of the copolymer and the lower one to the PS block. All the blends show two separate peaks, and as the SAN composition increases in the blend, the upper peak (PMMA block) shifts to lower temperature and the peak depth increases. The lower one, however, became smaller in peak

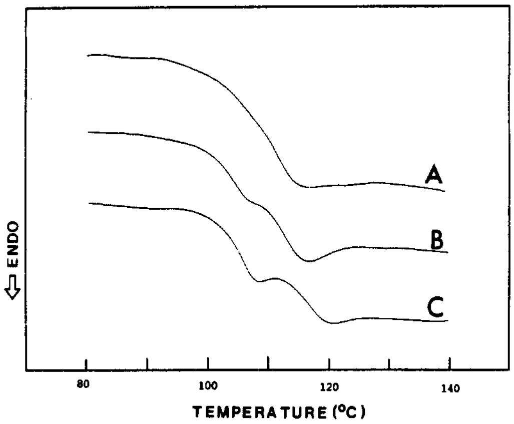

Figure 4. DSC thermograms of SAN/SbM binary blends: (A) 70/30 SAN/SbM; (b) 50/50 SAN/SbM; (C) 30/70 SAN/SbM.

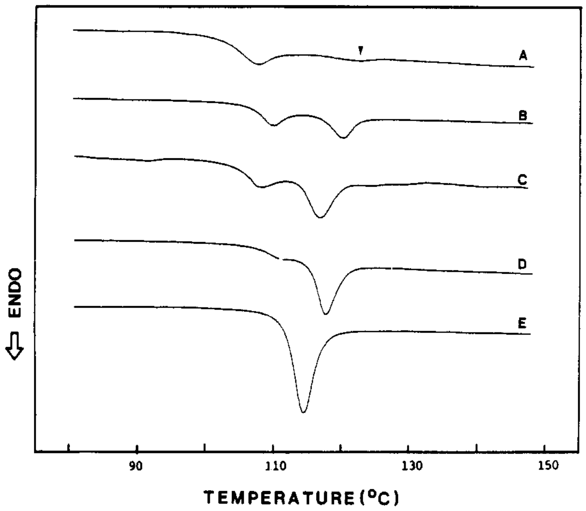

Figure 5. DSC thermograms of SAN/SbM binary blends as annealed at 82 °C for 145 h: (A) SbM; (B), 30/70 SAN/SbM; (C) 50/50 SAN/SbM; (D) 70/30 SAN/SbM; (E) SAN.

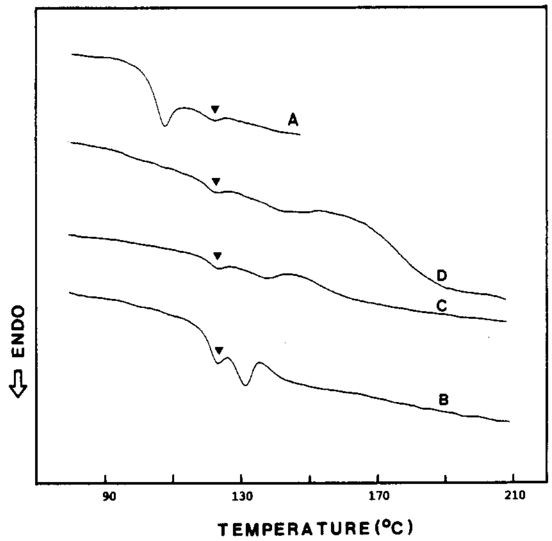

Figure 6. DSC thermograms of MPPO/SbM binary blends as annealed: (A) SbM; (B) MPPO/SbM; (C) 50/50 MPPO/SbM; (D) 70/30 MPPO/SbM.

depth and no significant shift could be observed.

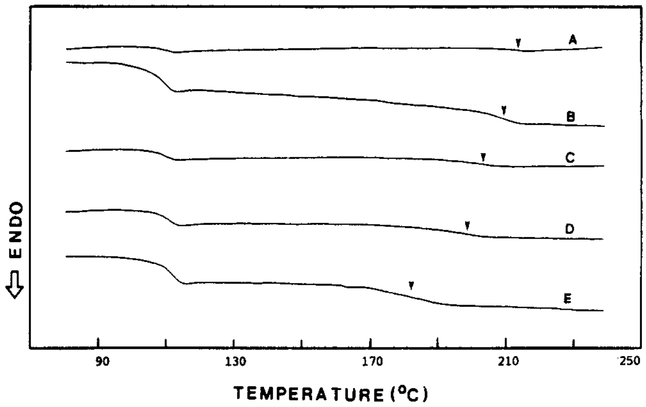

Figure 7. DSC thermograms of 50/50 MPPO/SAN blends: (A) 0% block copolymer; (B) 1% block copolymer added; (C) 4% block copolymer added; (D) 8% block copolymer added; (E) 15% block copolymer added.

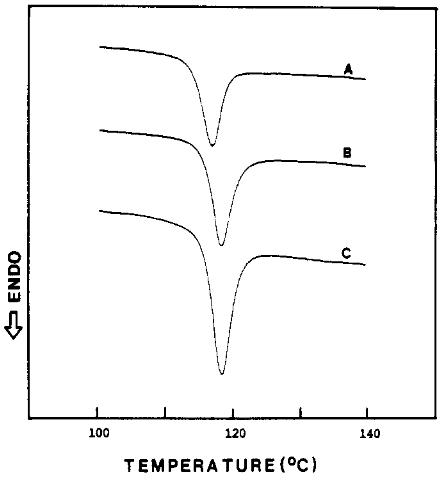

Figure 8. DSC thermograms of 50/50 MPPO/SAN blends as annealed: (A) 0% block copolymer; (B) 8% block copolymer added; (C) 15% block copolymer added.

DSC thermograms of annealed MPPO/block copolymer blends are shown in Figure 6. As compared with Figure 5, the peak for the PMMA block of the copolymer exhibited no change, while the peak or corresponding T_g of the PS block shifted to higher temperature. Thus it is considered that the higher peak or T_g of these blends (Figure 6B–D) corresponds to the MPPO/PS phase and the lower one to the PMMA phase. As mentioned above, all binary blends showed a two-phase structure; that is, one segment of the block copolymer formed a homogeneous phase with a miscible polymer and the other a phase of its own.

Figure 7 shows the glass transition temperature of 50/50 MPPO/SAN blends. Without block copolymer (Figure 7A), two distinct T_g's corresponding to those for the parent polymers are observed, indicating they are immiscible. When the block copolymer is added to the blend, it is observed that the upper T_g shifts to lower temperature while the lower T_g remains unchanged. The upper T_g corresponds to the phase composed of the MPPO/PS block, and more PS block is dissolved in MPPO domains as the amount of block copolymer increases. The unchanged lower T_g, however, corresponds to the phase composed of the SAN/PMMA block, recalling that the difference of their glass transition temperatures is small. It is very difficult to see exactly the phase corresponding to the lower T_g from Figure 7. Hence a physical aging technique was employed. When the sample is annealed, the lower part of the annealed blends shows a single sharp peak (Figure 8), indicating that the SAN/PMMA block forms a homogeneous phase. The above results reveal that all ternary blends involving a block copolymer have a two-phase structure: the PS block and MPPO form one phase, and the PMMA block and SAN form the other phase. Consequently, it is believed that the location of the block copolymer is at the interface of the two immiscible polymers, MPPO and SAN, suggesting that the block copolymer plays a proper role as a compatibilizing agent in the present system.

Summary

The compatibilizing effect of a styrene–methyl methacrylate block copolymer on the blends of two immiscible polymers, MPPO and SAN, was investigated by means of scanning electron microscopy and thermal analysis. The blends showed a two-phase structure, and the location of the block copolymer in the blend is considered as the interface. Upon addition of only a small amount (ca. 1 wt %) of block copolymer, the blends exhibit a more regular and finer dispersion. One of the important parameters for emulsifying efficiency of AB block copolymer to polymers A and B is the molecular weight of the individual segments. Riess et al.[21,22] have found that an effective interfacial agent requires the ratio of molecular weights of homopolymers to the corresponding blocks of copolymer to be equal to or less than one. In the present system, however, it is noteworthy that the ratio of molecular weights of SAN to PMMA block was much greater than one. We believe that this value stems from an exothermic enthalpy of mixing of each polymer with the corresponding block of copolymer, giving an additional thermodynamic driving force for solubilization.

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